

CLAIMS

1. A method of producing a fine particle material comprising
 - introducing one or more substances contained, such as dissolved and/or
5 dispersed in one or more fluid(s) into a vessel by introducing said fluid(s) into the vessel, said vessel containing one or more section(s) comprising a material, at least one of the fluids being in a supercritical state before or after being introduced into said vessel,
 - causing and/or allowing, said substances to precipitate at least partly as primary
10 particles on the surface of said material.
2. A method according to claim 1, wherein the average diameter of said nanoscaled primary particles is smaller than 100 nanometer such as smaller than 30 nanometer, preferably smaller than 20 nanometer, and even more preferable below 15 nanometer
15 such as below 10 nanometer
3. A method according to any of the claims 1-2, wherein the standard deviation of the size distribution of said primary particles formed is less than 60 % of the average diameter of said primary particles, such as 40 % of the average diameter of said primary particles,
20 and preferable less than 30 % of the average size of said primary particles, and even more preferable less than 20 % of the average size of said primary particles such as less than 15 % of the average size of said primary particles.
4. A method according to any of the claims 1-3, wherein the standard deviation of the
25 size distribution of said primary particles formed is maximum 20 nanometer, such as maximum 10 nanometer, and preferably less than 5 nanometer, and even more preferably less than 3 nanometer.
5. A method according to any of the claims 1-4, wherein at least one of said fluid(s)
30 being in a supercritical state is selected from the group consisting of carbon dioxide, alcohols such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol, pentanol, hexanol, water, methane, ethane, propane, butane, pentane, hexane, cyclohexane, heptane, ammonia, sulfurhexafluoride, nitrous oxide, chlorotrifluoromethane, monofluoromethane, acetone, THF, acetic acid, citric acid, ethylene glycol, polyethylene
35 glycol, N,N-dimethylaniline and mixtures thereof
6. A method according to claim 5, wherein one of the fluids is CO₂.
7. A method according to claim 5, wherein one of the fluids is an organic solvent.

8. A method according to any of claim 5, wherein one of the fluids is water.
9. A method according to any of the preceding claims, wherein the pressure of at
5 least one of said fluids is in the range 85-500 bar, preferably in the range 85-500 bar,
such as in the range 100-300 bar.
10. A method according to any of the preceding claims, wherein the temperature in the
vessel is maintained in the range 20-500 °C, such as 30-450 °C, and preferable in the
10 range 35-200 °C, and more preferable in the range 40-150 °C.
11. A method according to any of the preceding claims, wherein said fluid further
comprises at least one co-solvent.
- 15 12. A method according to claim 11, wherein the co-solvent is selected from the group
consisting of alcohol(s), water, ethane, ethylene, propane, butane, pentane, hexane,
heptane, ammonia, sulfurhexafluoride, nitrous oxide, chlorotrifluoromethane,
monofluoromethane, methanol, ethanol, propanol, isopropanol, butanol, pentanol,
hexanol, acetone, DMSO, THF, acetic acid, ethyleneglycol, polyethyleneglycol, N,N-
20 dimethylaniline and mixtures thereof.
13. A method according to any of the preceding claims, wherein fluid further comprises
one or more surfactants, said surfactants being preferably selected from the group
consisting of hydrocarbons and fluorocarbons preferably having a hydrophilic/lipophilic
25 balance value of less than 15, where the HLB value is determined according to the
following formula: $HLB = 7 + \text{sum}(\text{hydrophilic group numbers}) - \text{sum}(\text{lipophilic group numbers})$.
14. A method according to any of the claims 1-13, wherein said precipitation is
30 provided/caused by a change in the solubility of at least one of said substances.
15. A method according to claim 14, wherein said change in the solubility is
provided/caused by an antisolvent present in the vessel.
- 35 16. A method according to claim 14, wherein said antisolvent is one of the fluids being
introduced to the vessel.

17. A method according to any of the claims 14-16, wherein said change in solubility of at least one of said substances is provided/caused by expanding at least one of said fluids containing at least one of said substances into the vessel.

5 18. A method according to any of the claims 14-17, wherein said change in solubility is provided/caused by a change in the temperature of said fluid(s).

19. A method according to any of the preceding claims, wherein at least one of said substances undergoes a chemical reaction.

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20. A method according to claim 19, wherein said chemical reaction(s) is/are a sol-gel reaction(s).

21. A method according to claim 20, wherein the maximum temperature in the vessel
15 during said sol-gel reaction(s) is maintained below 400 C, such as below 300 C, preferably below 250 C such as below 200 C, and even more preferably below 150 C such as below 100 C.

22. A method according to claims 19-21, wherein at least one said substances
20 undergoing a chemical reaction is a sulphate salt or a halide such as a chloride.

23. A method according to claims 19-21, wherein at least one said substances undergoing a chemical reaction is an alkoxide.

25 24. A method according to claim 23, wherein said alkoxide comprises a metal- or semi-metal alkoxide.

25. A method according to claim 24 comprising:

30 i. introducing into the vessel at least one of said reactant(s) and/or precursor(s) and/or initiator(s) and/or catalyst(s) for said chemical reaction

35 ii. subsequently introducing into the vessel one or more substances dissolved and/or dispersed in at least one fluid.

iii. and vice versa

26. A method according to claim 25, comprising multiple subsequent steps of
- iv. introducing into the vessel at least one of said reactant(s) and/or precursor(s) and/or initiator(s) and/or catalyst(s) for said chemical reaction
 - v. subsequently introducing into the vessel one or more substances dissolved and/or dispersed in at least one fluid.
 - vi. and vice versa
27. A method according to claim 26, wherein said material in said one or more section(s) is capable of adsorbing at least one of said reactant(s) and/or precursor(s) and/or catalyst(s) on said material.
28. A method according to claim 27, wherein said reactant(s) and/or precursor(s) and/or catalyst(s) is/are adsorbed substantially in a monolayer of said material.
29. A method according to any of the claims 19-28, wherein the time for said chemical reaction(s) is less than 24 hours, such as less than 12 hours and preferable less than 8 hours, and even more preferable less than 4 hours.
30. A method according to any of the claims 19-28, wherein the time for said chemical reaction(s) is maximum 2 hours, such as maximum 1 hour, preferably less than 30 minutes and even more preferably less than 15 minutes.
31. A method according to any of the preceding claims, wherein said material present in said one more section(s) of said vessel, provides a distributing effect of said fluid(s) being introduced into said vessel.
32. A method according to claim 31, wherein the fraction of the total volume comprised by the said material in said one or more section(s) is up to 70 %, such as up to 50 %, preferably up to 30 %, and even more preferably up to 20 %.
33. A method according to any of the preceding claims, wherein said material present in said one or more section(s) of said vessel, comprises additional nucleation sites.
34. A method according to any of the preceding claims, wherein said material present in said one or more section(s) of said vessel, provides a seeding effect.

35. A method according to claim 33, wherein the number of nucleation sites is further increased by introducing an ultrasound and/or a vibrating surface effect.

5 36. A method according to any of the claims 33-35, wherein said material present in said one or more sections is a template for forming said primary particles into a specific shape, size, structure or phase.

37. A method according to claim 36, wherein said primary particles being produced is a
10 least partly crystalline.

38. A method according to claim 35-37, wherein said seeding effect is at least partly provided by seed particles.

15 39. A method according to claim 38, wherein said seed particles is in a fluidised or suspended state.

40. A method according to the claims 38-39, wherein said seed particles comprises the same material as said primary particles.

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41. A method according to any of the claims 31-40, wherein said material present in said one or more sections comprises a porous structure such as a sheet, a spongy or a grid structure.

25 42. A method according to any of the claims 31-40, wherein said material present in said one or more sections is a fibrous material.

43. A method according to claims 41-42, wherein said material present in said one or more sections has/have a hydrophilic surface.

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44. A method according to claims 41-42, wherein said material present in said one or more section has/have a hydrophobic surface.

45. A method according to any of the claims 41-44, wherein said material is a polymer
35 material.

46. A method according to claim 45, wherein the material in the vessel is a polymer or elastomer such as selected from the group consisting of polyethylene, polypropylene, polystyrene, polyesters, polyethylene terephthalate, polyvinyl chloride, polyvinyl acetates,

polyoxymethylene, polyacryloamide, polycarbonate, polyamides, polyurethane, copolymers thereof, chlorinated products thereof, rubbers and chlorinated rubber, silicone rubbers, butadiene rubbers, styrene-butadiene-rubbers, isoprene polymers, vulcanised fluororubbers, silicone rubbers.

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47. A method according to any of the claims 46, wherein said polymer material is polypropylene.

48. A method according to claim 45, wherein said fibrous material is an elastic
10 material.

49. A method according to any of the claims 41-44, wherein said material is a ceramic material.

15 50. A method according to claim 49, wherein said material is a glass wool such as quartz wool.

51. A method according to claim 49, wherein said material is an aerogel.

20 52. A method according to claim 51 comprising the steps of
- producing said aerogel material by a sol-gel reaction in an organic solvent
- removing said organic solvent by extraction in supercritical CO₂
- drying at least partly said aerogel
- forming said primary particles on the surface of said aerogel by a method
25 according to any of the preceding claims.

53. A method according to any of the claims 41-52, wherein the specific surface area (m²/m³) of said material in said sections is above 500 m²/m³, such as 1000 m²/m³, such as above 10.000 m²/m³, and preferably above 50.000 m²/m³ such as above 100.000 m²/m³.
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54. A method according to claim 53, wherein said material is a filtration medium.

55. A method according to any of the claims 53-54, wherein said material present in said one or more sections in the vessel further comprises at least one hollow tubular
35 member comprising an inner and an outer surface, and having at least one end communicating with the outside of said vessel, at least part of said hollow tubular member(s) comprising a membrane, at least one of the fluids being introduced into the vessel through the membrane.

56. A method according to claim 55, wherein said hollow tubular member(s) is blocked in the one end being inside the vessel.

57. A method according to claim 56, wherein both ends of said hollow tubular member(s) are open and are communicating with the outside of said vessel.

58. A method according to claim 57, wherein said membrane contains at least one dense layer.

59. A method according to any of the preceding claims 55-58, wherein said membrane is a porous membrane, preferably being a membrane having pores within a range of 0,001-100 micron, such as a pores in the range 0,01-10 micron, and preferably being a membrane having pores within the range of 0,01- 0,1 micron.

60. A method according to any of the claims 55-59, wherein the inlet end of said hollow tubular member(s) is communicating with an inlet plenum, wherein an antisolvent is introduced, at least part of said antisolvent permeating said membrane surface and providing a controlled and uniform distribution of said antisolvent in said vessel.

61. A method according to any of the claims 59-60, wherein at least one of said fluids containing dissolved substances is introduced into the vessel through said hollow tubular member(s).

62. A method according to any of the claims 60 or 61, wherein at least two fluid streams are introduced into the vessel through two separate sets of hollow tubular member(s) each having an inlet plenum communicating with the outside of the vessel.

63. A method according to any of the claims 61-62, comprising contacting at least part of the inner surface of said hollow tubular member(s) with a first fluid, and contacting at least part of the outer surface(s) of said hollow tubular member(s) with a second fluid, a least part of said first fluid permeating through at least part the wall(s) of said hollow tubular member(s), and mixes with said second fluid substantially at the outer surface(s) of said hollow tubular member(s).

64. A method according to claim 63, wherein a micro-emulsion of said first fluid in said second fluid is formed.

65. A method according to any of the claims 61-64, wherein one of the fluids is water or contains water.

66. A method according to claim 65, wherein said water or water mixture contains one or more substances preferably being dissolved or dispersed therein.

5 67. A method according to any of the claims 61-66, wherein one of the fluids is CO₂ or an oil.

68. A method according to claim 67, wherein said fluid further comprises one or more surfactants.

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69. A method according to any of the claims 64-68, wherein said microemulsion formed comprises a water core.

70. A method according to claim 69, wherein said water core comprises dissolved
15 and/or dispersed substances.

71. A method according to the claims 69-70, wherein the diameter of said water core in said emulsions formed is in the range 0,5-15 times the diameter of the pores of the membrane part of said hollow tubular member(s) contacting said second fluid, such as in
20 the range 1-10 times the diameter of the pores of the membrane part of said hollow tubular member(s) contacting said second fluid, and preferably in the range 2-4 times the diameter of the pores of the membrane part of said hollow tubular member(s) contacting said second fluid.

25 72. A method according to any of the claims 65-71, wherein said material present in said one or more sections, comprises two sets of hollow tubular member(s), both sets of said hollow tubular member(s) comprising a plenum and an outlet plenum communicating with the outside of said vessel, and wherein two different fluids can be contacted with the inner surface of said hollow tubular member(s), and where two different emulsion(s) of
30 said fluids in said fluid contacting the outer surface of said hollow tubular member(s) are formed.

73. A method according to any of the claims 65-72, wherein a reaction is occurring in said microemulsion(s).

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74. A method according to any of the claims 65-73, wherein said fluid containing said microemulsion(s) are used to dissolve and/or extract substances outside of said vessel.

75. A method according to any of the preceding claims, wherein said vessel is operating at a substantially constant pressure, such as operating continuously at a constant pressure during pre-selected time intervals.
- 5 76. A method according to any of the preceding claims, wherein said vessel is at a substantially constant pressure at more than one subsequent pre-selected pressure levels.
77. A method according to any the preceding claims, comprising re-circulating in at least part time of the method at least part of a fluid mixture present in the vessel, the re-
10 circulating comprising:
- withdrawing from the vessel at least a part of a fluid from the vessel and feeding it to a re-circulation loop and subsequently feeding the fluid back to the vessel.
- 15 79. A method according to claim 77, further comprising the step of controlling the temperature of the fluid in the re-circulation loop.
80. A method according to any of the claims 77-78, wherein heat is added and/or extracted from the fluid in the re-circulation loop.
- 20 81. A method according to any of the claims 77-79, wherein one or more reactant is added and/or extracted from the fluid in the re-circulation loop.
82. A method according to 80, wherein at least one of the reactants is an alcohol an
25 alkoxide and/or water.
83. A method according to claim 81, wherein a metal- or semi-metal alkoxid are produced in-situ in the process prior to being introduced to said vessel by said fluid.
- 30 84. A method according to any of the preceding claims, wherein the method comprises controlling the temperature- and/or pressure- and/or density- and/or concentration profiles within the vessel.
85. A method according to any of the preceding claims, wherein the temperature
35 profile within the vessel is controlled by controlling the temperature and flow rate of at least one fluid flowing inside said hollow tubular members.

86. A method according to any of the preceding claims, wherein said material present in said one or more sections in vessel with said precipitated primary particles thereon comprises the final product.

5 87. A method according to claim 85, wherein said product comprises primary particles deposited on a carrier film such as a tape cast.

88. A method according to claim 85, wherein said primary particles on said surface of said material constitutes a film or a coating.

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89. A method according to claim 87, wherein said film or coating has one or more layer(s) each layer having a layer thickness of up to 1 micron, such as a layer thickness below 500 nanometer, preferable a layer thickness below 250 nanometer such as a layer thickness below 100 nanometer. Even more preferable the layer thickness of said film is
15 below 50 nanometer, such as a layer thickness below 30 nanometer.

90. A method according to any of the claims 87-88, wherein said coating comprises multiple layers.

20 91. A method according to claim 89, where the layers comprises different materials.

92. A method according to any of the claims 87-90, wherein said product is further subjected to an annealing process.

25 93. A method according to claim 91, wherein said annealing is performed by microwaves.

94. A method according to claim 85, wherein said primary particles are deposited on the surface of said material in the form of small clusters of individual particles, and
30 preferably as individual particles.

95. A method according to claim 93, wherein said clusters comprises up to 100 atoms , such as up to 50 atoms, and preferably less than 10 atoms, and even more preferably less than 5 atoms.

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96. A method according to any of the claims 93-94, wherein said clusters or individual particles on the surface of said material are deposited as quantum dots.

97. A method according to any of the preceding claims, wherein said primary particles precipitated on said surface of the material present in said one or more section(s) are removed from said material as a powder.
- 5 98. A method according to claim 96, wherein said powder consists of weakly bounded agglomerates of primary particles.
99. A method according to claim 97, wherein said powder has weakly bounded agglomerates of a size of maximum 10 micron, such as up to 5 micron, and preferably up
10 to 1 micron such as up to 500 nanometer.
100. A method according to any of the claims 96-98, wherein said powder is removed from said material by introducing a vibrating effect and/or an acoustic effect such as ultrasound waves and/or by back flushing and/or by applying an pressure pulse effect.
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101. A method according to claim 99, wherein said vibrating effect is generated by piezoelectric means.
102. A method according to claim 99, wherein said vibrating effect is generated by a
20 magneto-restrictive means.
103. A method according to any of the claims 96-101, wherein said powder is removed from said material while said material is within the vessel.
- 25 104. A method according to claim 102, wherein said removal of said powder are performed according to a back flush or back pulse or a back chock technique.
105. A method according to any of the claims 102-103, wherein said removed powder are withdrawn from the vessel by flushing with a fluid or fluid mixture present in the
30 vessel.
106. A method according to claim 104, wherein said fluid containing said formed powder is fed into a second vessel containing a liquid.
- 35 107. A method according to any of the claims 104-105, wherein said fluid containing said formed powder is expanded into said liquid thereby providing said formed powder material as a dispersion in said liquid.

108. A method according to claim 104, wherein said fluid containing said formed powder is fed to a bag filter or ceramic filter for separation of said formed powder material from the fluid.

5 109. A method according to claim 104, wherein said fluid containing said formed particulate material is fed to a membrane separation device.

110. A method according to claim 104, wherein said formed powder contained in said fluid is deposited on to a second solid in a second vessel.

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111. A method according to claim 109, wherein said deposition is performed by spraying.

112. A method according to any of the preceding claims, wherein said precipitated
15 primary particles on said material are exposed to one or more coating or encapsulation steps and/or reaction steps with one or more materials.

113. A method according to claim 111, wherein said coating or encapsulation step(s) is performed within the vessel.

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114. A method according to any of the claims 111-112, wherein said coating or encapsulation step(s) is performed at least partly during harvesting/removing said particles from said material.

25 115. A method according any of the claims 111-113, wherein said coating or a further coating is performed in a second vessel.

116. A method according to any of the preceding claims, wherein said nanomaterial production process involves one of the following processes: RESS (rapid expansion of
30 supercritical solutions), GAS (Gas Antisolvent), SAS (solvent Anti Solvent), SEDS (Solution Enhanced Dispersion by supercritical fluid), PCA (Precipitation with Compressed Antisolvent), PGSS (Precipitation from Gas-saturated Solutions) and variations thereof.

117. A method according to any of the preceding claims, wherein said primary particles
35 comprises an electro-ceramic material.

118. A method according to any of the preceding claims, wherein said primary particles comprises a semi-conducting material.

119. A method according to any of the preceding claims, wherein said primary particles comprises a magnetic, ferromagnetic, paramagnetic, or superparamagnetic material.

120. A method according to any of the preceding claims, wherein said primary particles
5 comprises a core-shell structure.

121. A method according to any of the preceding claims, wherein said core comprises a magnetic or ferro magnetic core.

10 122. A method according to any of the preceding claims, wherein said primary particles comprises a piezoelectrical material.

123. A method according to claim 121, wherein said piezoelectrical material comprises lead zirconate titanate, $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$

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124. A method according to any of the preceding claims, wherein said primary particles comprises oxide(s), oxyhydroxide(s), hydroxide(s) such as metal oxide(s), semi-metal oxide(s), metal oxyhydroxide(s), semi-metal oxyhydroxide(s), metal hydroxide(s), semi-metal hydroxides and combinations thereof.

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125. A method according to any of the claims 116-123, wherein said oxides comprises oxides of one or more of the following elements: Al, Si, Ti, Zr, Zn, Fe, Ni, Co, Ce, Ge, Ba, Sr, W, La, Ta, Y, Mn, V, Bi, Sn, Te, Se, Ga, Be, Pb, Cr, Mg, Ca, Li, Ag, Au, Pt, Pd, Cd, Mo, Eu and combinations thereof.

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126. A method according to claim 124, wherein said oxides is selected among silica, alumina, zirconia, titania and combinations thereof.

127. A method according to any of the claims, wherein said primary particles comprises
30 carbide(s) and/or nitride(s).

128. A method according to any of the claims 123-124, wherein said metal or semi-oxide(s) is/are precursor(s) for a thermoelectric material.

35 129. A method according to claim 127, wherein said precursor(s) is/are reduced in the process by adding a reducing agent to form a thermoelectric material.

130. A method according to claim 128, wherein said thermoelectric material formed comprises a clathrate.

131. A method according to any of the claims 127-129, said thermoelectric material comprises one or more of the elements: Ba, Bi, Te, Se, Zn, Sn, Sr, Ga, Ge, Pb, Cd, Sb, Ag, Si and combinations thereof.

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132. A method according to claim 130, further comprising doping said primary particles of said thermoelectric material with metals and/or semi-metals.

133. A method according to claim 131, wherein said thermoelectrical material have a thermal conductivity at temperatures above 20 C of maximum 10 watts per meter Kelvin, such as maximum 5 watts per meter Kelvin, preferably maximum 3 watts per meter Kelvin such as maximum 1,5 watts per meter Kelvin, and even more preferably a heat conductivity of maximum 1 watt per meter Kelvin.

15 134. A method according to any of the preceding claims, wherein said primary particles comprises one or more pharmaceutical and/or biological material(s).

135. A method according to any of the preceding claims, wherein said primary particles deposited on the surface of said surface provides an antibacterial effect of said surface.

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136. A method according to any of the preceding claims, wherein said material comprises a high surface area material.

137. An apparatus comprising one or more of the means disclosed in any of the preceding claims and being adapted to carry out the method according to any of the preceding claims.

138. A product obtainable according to a method in any of the preceding claims.

30 139. A tape cast for tape casting, comprising primary particles deposited on a carrier film, wherein said primary particles have:

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- a. an average diameter of less than 100 nanometer such as an average diameter of less than 30 nanometer, preferably an average diameter of smaller than 20 nanometer and even more preferable an average diameter below 15 nanometer such as below 10 nanometer.
 - b. a narrow size distribution around the average diameter characterized by having a maximum standard deviation of said distribution of maximum 20 nanometer, such as maximum 10 nanometer, and preferably less than 5

nanometer.

140. A tape cast according to claim claim 138, suitable for production of a ceramic material by tape casting.

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141. A tape cast according to claim 139, wherein the sintering temperature is maximum 1100 C, such as maximum 1000 C, and preferable maximum 900 C, and even more preferably maximum 800 C, such as 700 C.

10 142. A tape cast according to claim 140, wherein the material being produced is a piezomotor produced from lead zirconate titanate tape cast.

143. An item having a hard nanocrystalline coating comprising primary particles of Al_2O_3 and ZrO_2 according to any of the preceding claims, wherein said coating has a hardness of
15 at least 10 GPA, such as a hardness of at least 15 GPA, and preferably above 20 GPA, and even more preferably a hardness of at least 25 GPA.

144. An item having a hard nanocrystalline coating comprising primary particles of Al_2O_3 and ZrO_2 according to any of the preceding claims, wherein said coating has a scratch and
20 wear resistance of at least 30 N, such as a scratch and wear resistance of at least 35 N, preferably a scratch and wear resistance of at least 40 N, and even more preferably a scratch resistance of at least 45 N.

145. An item having a hard nanocrystalline coating according to any of the claims 142-
25 143, further comprising primary particles of ZnO .

146. A hard nanocrystalline coating according to any of the claims 142-144, wherein said coating is applied to a polymer or a glass material.

30 147. A mechanical part with a hard nanocrystalline coating according to any of the claims 142-145, wherein said coating is applied to the surface of said material.